## EXHIBIT A

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# Nomenclature and Simple Reactions of the Hydrocarbons

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The simplest organic molecules, those containing only carbon and hydrogen, are called hydrocarbons. The least complex of these have only single carbon-carbon bonds, and are said to be *saturated*. Molecules having no rings of carbon atoms are referred to as *aliphatic*, and the saturated aliphatic hydrocarbons are called *alkanes*. Saturated hydrocarbons with one or more rings are called cycloalkanes.

### Nomenclature and Physical Properties of Saturated Hydrocarbons

#### THE ALKANES

Organic chemists think of the alkanes as a carbon skeleton holding a sheath of hydrogen atoms. The simplest skeletal pattern is a continuous—that is, nonbranched—chain of carbon atoms. In Table 3–1 are shown the structures, names, and basic physical properties of the first twenty alkanes with continuous (normal, n-) chains. Note that these like all alkanes have the empirical formula  $\mathbf{C}_n\mathbf{H}_{2n+2}$ .

Although there is no difficulty in naming the normal alkanes (for those who know the Greek numbers), problems quickly arise with the various branched-chain skeletons. Early chemists gave special names to each skeletal pattern, such as iso for the single carbon branch next to the end of a chain. This suffices for the two butanes, and with the addition of the prefix neo-, the three pentanes can be handled.

$$\textbf{CH}_{3}\textbf{---}\textbf{CH}_{2}\textbf{---}\textbf{CH}_{3}$$

However, things rapidly get out of hand with five hexanes or eight heptanes to be named. Clearly what is needed is a system using a minimum number of rules to name the maximum number of skeletal patterns.

Table 3-1. Structure, Names, and Physical Properties of n-Alkanes.

Structure	Name	m.p., °C .	b.p., °C
ĜH <sub>i</sub>	methane	_183	:-162
CH3CH3	ethane	—172	_89
CH3—CH2—CH3	propane	—187	_42
CH3—CH2—CH2—CH3	л-butane	135	
CH3—(CH2)3—CH3	n-pentane	130	
ĞH₃—(CH₂)₄—CH₃	n-hexane	— 94	69
GH₃—(CH₂)₅—GH₃	n-heptane	- — 91	98
CH₃—(CH₂)₅—CH₃;	n-octane	57	1,26
GGH₃—(CH₂);—CH₃	n-nonane	54	1,51
CH <sub>3</sub> —(CH <sub>2</sub> ) <sub>3</sub> —CH <sub>3</sub>	n-decane	=30	174
CH <sub>3</sub> —(CH <sub>2</sub> ) <sub>3</sub> —CH <sub>3</sub>	n-undecane	=26	196
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> -CH <sub>3</sub> CH <sub>3</sub> - (CH <sub>2</sub> ) <sub>11</sub> - CH <sub>3</sub>	n-dodecane n-tridecane	—10 —6 ~6	216 230 251
CH <sub>3</sub> =(CH <sub>2</sub> ) <sub>12</sub> =CH <sub>3</sub>	n-tetradecane	* 10	268
CH <sub>3</sub> =(CH <sub>2</sub> ) <sub>13</sub> =CH <sub>3</sub>	n-pentadecane	* 18	280
CH <sub>3</sub> —(CH <sub>2</sub> ) <sub>14</sub> —CH <sub>3</sub>	n-hexadecane	22	303
CH <sub>3</sub> —(CH <sub>2</sub> ) <sub>15</sub> —CH <sub>3</sub>	n-heptadecane	28	308
CH <sub>3</sub> —(CH <sub>2</sub> ) <sub>16</sub> —CH <sub>3</sub>	n-octadecane	32	330
CH <sub>3</sub> —(CH <sub>2</sub> ) <sub>17</sub> —CH <sub>3</sub>	n-nonadecane	36	
	n-eicosane		

IUPAC System. Recognizing this need a group of chemists met in Geneva in 1892 and devised the initial rules. Adopted by the International Union of Pure and Applied Chemistry (IUPAC) this system has been revised periodically, most recently in 1957. The basis of the system is to treat each

<sup>&</sup>lt;sup>e</sup>The 1957 IUPAC rules have been published in an English version as, Nomenclature of Organic Chemistry. London: Butterworths Scientific Publications, 1958.

structure as derived from a simple skeleton by appropriate modifications. Each systematic name has three parts:

- 1. A root which indicates the nature of the basic skeleton
- 2. A suffix which designates the most important functional groups in the molecule.
- 3. A series of prefixes which describe the modifications made in the basic skeleton to form the structure in question.

Note how effectively this simple notion handles the problems of naming branched-chain alkanes. Branched-chain alkanes are named as derivatives of the longest chain normal alkane in the molecule. This means the basic skeleton is picked as the longest continuous chain of carbons in the molecule. The root of the name is the same as the root for the normal alkane having the same number of carbons as that longest chain: the suffix -ane is used to indicate a saturated hydrocarbon. For example, the following compound is named as a derivative of pentane:

$$^{1}$$
CH<sub>3</sub>— $^{2}$ CH<sub>2</sub>— $^{3}$ CH $^{4}$ CH<sub>2</sub>— $^{5}$ CH<sub>3</sub>

3-methylpentane

To complete the name we need only indicate by appropriate prefixes the kinds and positions of the branches attached to the basic skeleton. The basic chain is numbered consecutively from one end, the side chain is indicated by prefixing its name to the root, and its location is shown by hyphenating to this prefix the number of the carbon to which it is attached.

The names for some simple saturated side chains, derived from the alkanes by removal of one hydrogen, are listed in Table 3–2. These are called alkyl groups, and the symbol R— is often employed to denote a general alkyl group,  $C_nH_{2n+1}$ , in a structural formula.

If the main chain in a complex alkane has two or more different side chains attached, each is indicated by a separate prefix, each prefix being preceded by the proper locating number. When two like side chains are present (i.e., two methyls), the additional prefix di- is added (dimethyl) and the whole is preceded by two locating numbers, separated by a comma. For three like chains the addition tri- is used, for four tetra-, and so on. Illustrative examples follow.

$$\begin{matrix} ^{1}\text{CH}_{3} - \overset{2}{\text{CH}} - \overset{3}{\text{CH}}_{2} - \overset{4}{\text{CH}} - \overset{5}{\text{CH}}_{2} - \overset{6}{\text{CH}}_{3} \\ & \text{CH}_{3} & \text{CH}_{2} - \text{CH}_{3} \end{matrix}$$

2,2,3,3-tetramethylbutane

heptanes n number

kanes.

162 - 89 - 42 - 0 - 36 - 69 - 98 126 151 174 196 - 216 - 230 - 251 - 268

280

303

308

330

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4-ethyl-5-isopropyl-2,2dimethyloctane

Note that numbering of the main chain must always start from that end which gives the smaller set of locating numbers. In the last case, for example, the number set 2,2,4- must be used rather than the 2,4,4- which would result if numbers started at the other end.

At times the simple rule of finding the longest chain in the molecule does not uniquely determine a basic skeleton. For example, in the alkane having the carbon skeleton

two continuous chains of equal length (eight **C**'s) can be found. One runs horizontally across the page and the other is shown in brown. The rule used to decide cases like this says to pick the one that gives a maximum number of

Table 3-2. Formulas and Names for Some Simple Alkyl Croups.

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Structure	Name	Structure	Name
CH <sub>3</sub>	methyl	CH <sub>3</sub> —CH <sub>2</sub> —	ethyl
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	propyl	CH <sub>3</sub> —CH— .	isopropyl
		CH;	
CH3—CH3—CH3—CH2—	butyl :	GH;—GH—GH;	isobutyl
		CH <sub>3</sub>	
		CH;	
CH₃→CH→CH;→CH₃	sec-butyl	СН₃⊖С	fert-butyl or t-butyl
		CH₂	

dimethylbutyl

tane

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CH3 CH CH2 CH CH2 CH2 3,5-dimethylhexyl CH: CH<sub>3</sub> CH<sub>3</sub> 1,1,2-trimethyl-CH propyl CH<sub>3</sub> CH<sub>3</sub> 2-ethylbutyl CH -- CH CH3-CH2 CH2 CH<sub>3</sub> 1-ethyl-3,3-—CH₂— CH

Table 3-3. Official IUPAC Names for Alkyl Groups.

side chains. Thus the one in brown is the proper skeleton, and the correct name is 3-ethyl-2,7-dimethyl-5-propyloctane.

CH2—CH3

Not infrequently it becomes necessary to name alkyl groups more complex than those listed in Table 3-2. To do this the point of attachment is considered as the 1-carbon, and the longest continuous carbon chain starting from this point is used as the root name for the group. The suffix-yl is used to denote an alkyl group. Examples illustrating these naming procedures are shown in Table 3-3.

The student who reads beyond this book will soon discover that many chemists do not follow this official nomenclature for alkyl groups. These chemists prefer to use as the root name the longest chain that includes the point of attachment and to number this chain so as to give the point of attachment the smallest number possible. Using this scheme, the last case in Table 3-3 becomes 5,5-dimethyl-3-hexyl. Table 3-4 summarizes the important operational rules for naming alkanes.

#### THE CYCLOALKANES

Simple cycloalkanes pose no new problems in nomenclature. Only the additional prefix cyclo- is needed, the other rules being applied as before. The

Table 3-4. IUPAC Rules for Naming Saturated Hydrocarbons (in Operational Form).

- a. Find the longest continuous carbon chain in the molecule, and name as a derivative of the normal alkane having the same number of carbon atoms.
- b. Number that chain starting from the end that gives the smaller set of numbers.
- c. List the alkyl groups attached to the main chain (in alphabetical order) as a series of prefixes to the root name.
- d. Hyphenate to each radical name the number of the carbon of the basic skeleton to which it is attached.
- e. If a choice of two basic chains of equal length must be made, choose that one which gives a maximum number of simple side chains.

four simplest cycloalkanes are shown in Figure 3–1. Inveterate abbreviators, organic chemists do not normally write out all the carbon and hydrogen atoms in the rings, preferring to use the geometric figures shown adjacent to each formula in Figure 3–1. The general empirical formula for the cycloalkanes is  $C_nH_{2n}$ . Note that the cycloalkanes boil at slightly higher temperatures than the corresponding n-alkanes.

Structure	Name	b.p., °C
CH; CH2—CH2 ≡	cyclopropane	_33°
CH2—CH2     = CH2—CH2	cyclobutane	13°
CH₂ CH₂ CH₂ ≡	cyclopentane	49°
CH2—CH2 CH2 CH2—CH2		
CH <sub>2</sub> CH <sub>2</sub>	cyclohexane	81°

FIGURE 3-1. The simple cycloalkanes.

Cycloalkanes substituted with simple alkyl groups are named as derivatives of the parent cycloalkane, as is illustrated in the ensuing examples.

1-ethyl-3-methylcyclohexane

1,1-dimethylcyclobutane

tert-butylcyclopentane

For monosubstituted rings, such as *tert*-butyleyelopentane, no locating number is necessary. When a cycloalkane ring is attached to a complex alkylegroup, the molecule is named as an alkane with the cycloalkylegroup as a side chain.

3-cyclopentyl-2,5-dimethylhexane

## Nomenclature and Physical Properties of Unsaturated Hydrocarbons

Hydrocarbons containing one or more double or triple bonds are said to be *unsaturated*. Of the aliphatic unsaturated hydrocarbons, those with double bonds are called alkenes or olefins, while those with triple bonds are called alkynes or acetylenes.

#### THE ALKENES

The double bond in an alkene constitutes a functional group. A basic principle of the IUPAC system is that functional groups are to be given a preferred status in the naming of a compound. This extends to the choice of the basic carbon skeleton to use in naming the compound and to the numbering of that skeleton. In the case of the alkenes this leads to the following rules of nomenclature:

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pera-